Co-Optimization of
Fuels & Engines

Co-Optima Emissions, Emissions Control, and Merit Function Development

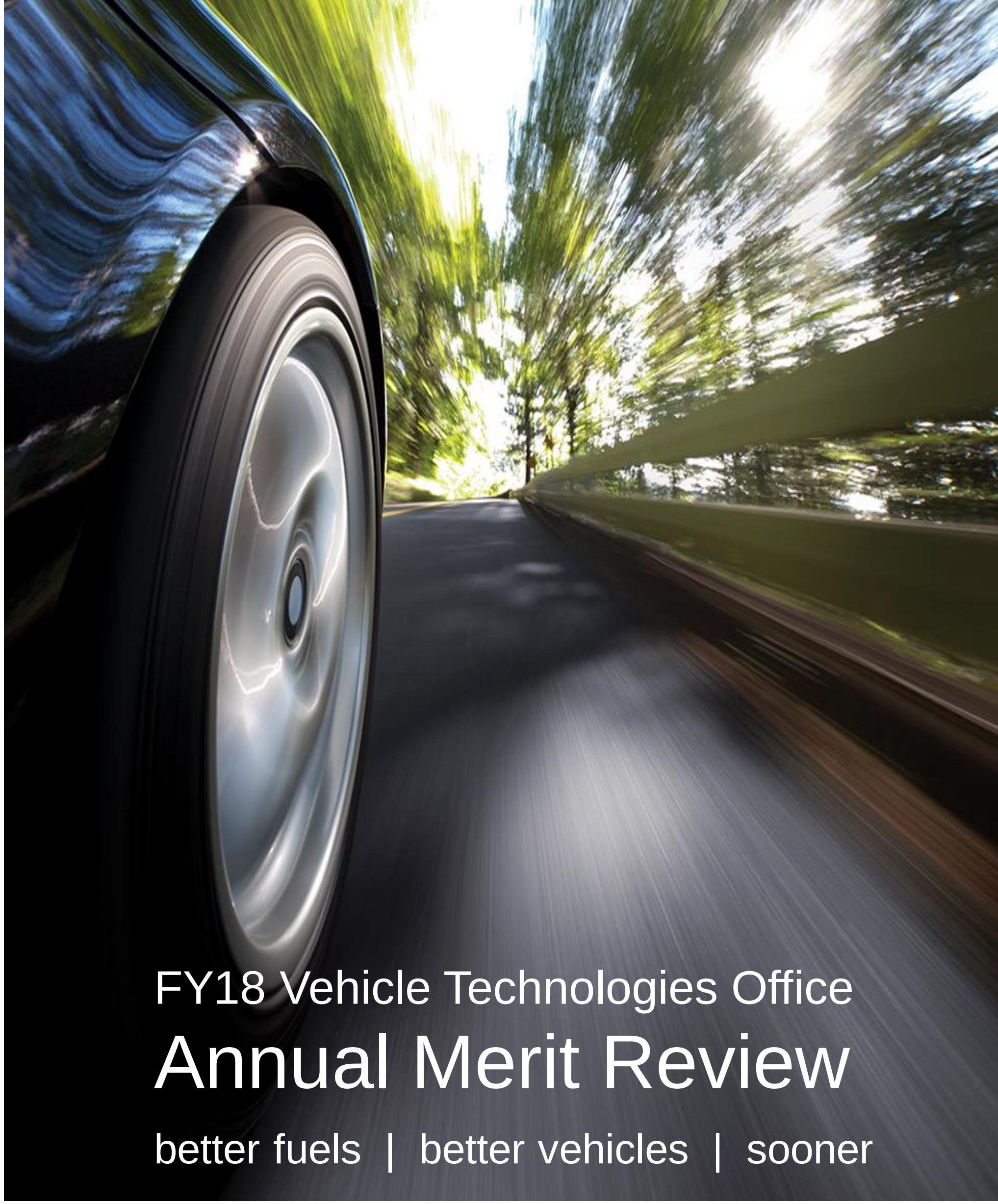
Presenter: Josh Pihl

PIs: Matt Ratcliff, Seonah Kim, Peter St. John, Melanie DeBusk, John Storey, Josh Pihl, Todd Toops, Chris Kolodziej, Bob McCormick, Paul Miles, Jim Szybist

VTO Program Managers: Gurpreet Singh, Kevin Stork, Michael Weismiller

Project # FT057

June 20, 2018



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Overview

Timeline

- Project start date: 10/1/2015
- Project end date: 9/30/2018*
- Percent complete: 88%

*Start and end dates refer to three-year life cycle of DOE lab-call projects, Co-Optima is expected to extend past the end of FY18

Budget

	FY16	FY17	FY18**
VTO	$1196k	$1196k	$745k
BETO			$235k

**As of April 2018 (under continuing resolution)

Barriers from ACEC Roadmap

- U.S. EPA Tier 3 Bin 30 emissions
- Reduced cold start emissions
- "…greater understanding of how new fuels impact advanced combustion strategies and aftertreatment systems"

Partners

- 9 DOE national laboratories
- 13 universities
- Co-Optima external advisory board
- Co-Optima stakeholders
  - 145 individuals
  - 86 organizations

Overview of tasks

Task		PI	Lab	FY18
F.1.6.1	Modification of PMI to Include Oxygenate Effects	Ratcliff	NREL	$70k
F.1.4.2	Predicting Sooting and Developing Quantum Skeletal Mechanisms for Soot and Autoignition **(BETO funded)**	Kim	NREL	$235k
E1.3.5	Study fuel impacts on ACI PM formation & complete study on impact on GDI PM	DeBusk/Storey	ORNL	$275k
E1.3.1	Fuel Impacts on Emissions Control Performance & Durability	Pihl/Toops	ORNL	$175k
E.2.3.1	Merit Function Development & Technical Roll-up	Kolodziej McCormick Szybist Miles	ANL NREL ORNL SNL	$60k $55k $55k $55k

Milestones: FY17

Task	Lab	Timing	Description of Milestone or Go/No-Go Decision	Status
F.1.6.1	NREL	FY17 Q1	Complete engine PM measurements with oxygenate fuel matrix designed to evaluate modifying PMI with YSI replacing DBE. Oxygenates to include some from LGGF team list as well as others intended to test hypothesis about oxygenate mechanistic pathways to form PM.	Complete
E.1.3.1	ORNL	FY17 Q4	Measure catalytic light-off behavior of at least five SI-HPF candidates (encompassing five different functional groups) over a three-way catalyst.	Complete

Milestones: FY18

Task	Lab	Timing	Description of Milestone or Go/No-Go Decision	Status
F.1.6.1	NREL	FY18 Q2	Draft journal article on the competing effects of HOV (from alcohol blending) and aromatics dilution on PM emissions and the impact of HOV on the LDSI merit function PM term	On track
F.1.4.2	NREL	FY18 Q3	Develop new predictive methods for sooting tendency from molecular structure using linear regression for both HC and oxygenated compounds derived from biomass	On track
E.1.3.5	ORNL	FY18 Q4	Complete PM sampling study on impact of fuels, T, and mixedness conditions on PM from mixed-mode SI/ACI	On track
E.1.3.1	ORNL	FY18 Q4	Measure TWC light-off temperatures for five fuel blends containing Co-Optima blendstocks to support evaluation of LD merit function term	On track
E.2.3.1	ANL	FY18 Q4	Expand ACI Merit Function to include 2-3 fuel properties	On track
E.2.3.1	SNL	FY18 Q4	Expand ACI Merit Function to include 2-3 fuel properties	On track
E.2.3.1	ORNL	FY18 Q4	Update diesel and ACI Merit Functions to reflect the known importance of fuel properties on efficiency for these combustion modes	On track

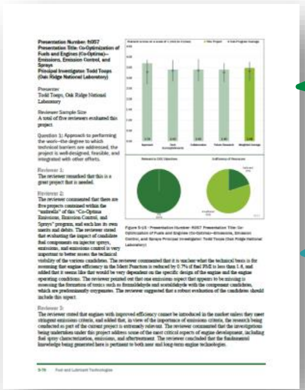
Relevance

- Internal combustion engines will dominate the fleet for decades and their efficiency can be increased significantly
- Research into better integration of fuels and engines is critical to accelerating progress towards economic development, energy security, and emissions goals
- Improved understanding in several areas is critical for progress:
  - fuel structure – property relationships
  - how to measure and predict key fuel properties
  - **the impact of fuel properties on engine performance and emissions**
- Research focused on key barriers to LD SI/multi-mode, MD/HD diesel, and ACI combustion approaches
- Research addresses VTO program plan knowledge gaps surrounding advanced combustion engine regimes and predicting the impact of fuel properties

LD = light duty; MD = medium duty; HD = heavy duty; SI = spark ignition; ACI = advanced compression ignition

Relevance of emissions control tasks to overall Co-Optima program

2017 Merit Review

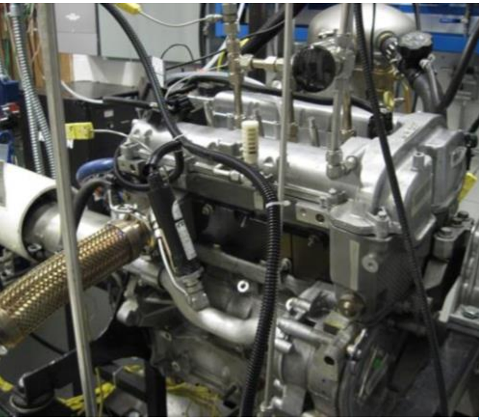


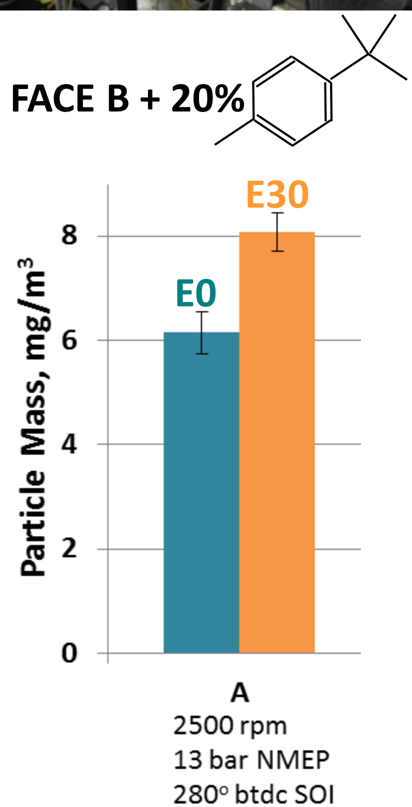
Reviewer 3: "…engines with improved efficiency cannot be introduced in the market unless they meet stringent emissions criteria… in view of the importance of emissions criteria, the research being conducted as part of the current project is extremely relevant

Reviewer 4: "…this project, especially the emphasis on fuel effects on exhaust aftertreatment, is extremely relevant… it is assumed that high-octane, high sensitivity fuels (fuel properties, not molecules) will yield high efficiency in SI, downsized, boosted gasoline engines, but what are unknown are the fuel effects on aftertreatment performance, because they are molecule dependent."

- Advanced engines running on high performance fuels still must meet emissions regulations
- Fuel chemistry impacts engine emissions (PM formation, HC speciation)
- Changes in fuel chemistry can introduce challenges & opportunities in emissions and emissions control
  - challenges & opportunities should be incorporated in co-optimization
- ***We need to understand how fuel chemistry impacts exhaust composition and performance of emission control devices to predict the effects of Co-Optima blendstocks on emissions compliance***

F.1.6.1: Modification of PMI to Include Oxygenate Effects





Matt Ratcliff, Jon Burton, Earl Christensen, Lisa Fouts, Stephen Burke, Bret Windom, Bob McCormick, Seonah Kim, Peter St. John (NREL)

Relevance:

- PMI can underpredict PM formation for oxygenates under certain operating conditions
  - ethanol can inhibit/delay aromatics evaporation via charge cooling, non-ideal vapor/liquid equilibria
- Boosted SI merit function contains PMI term to capture potential need for GPF
  - GPF can increase fuel consumption, cost

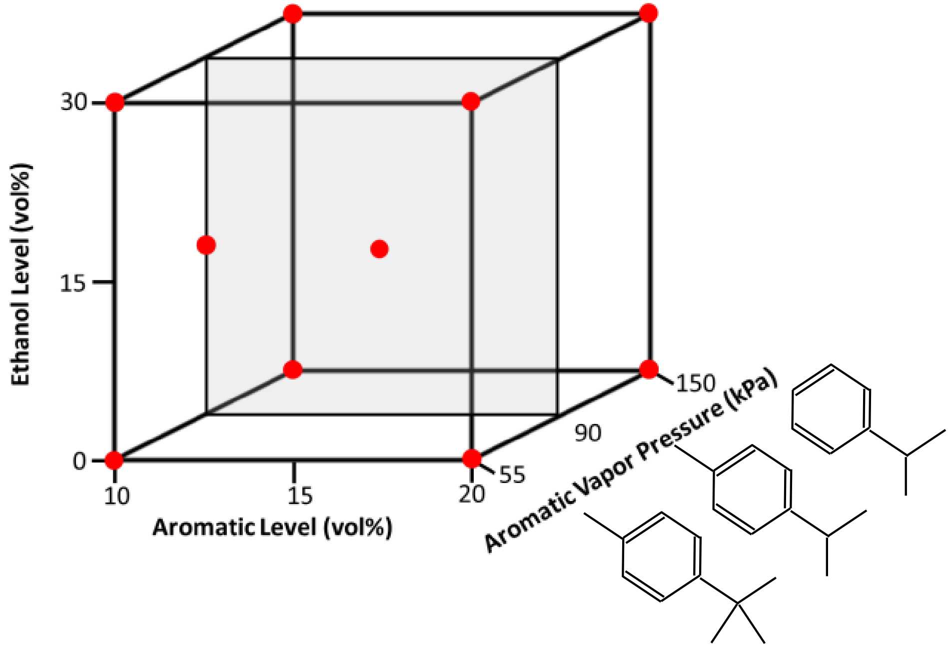
Objectives:

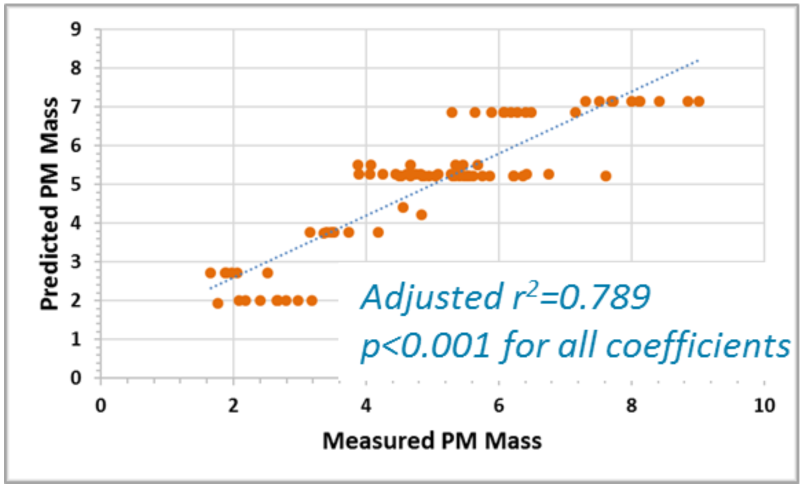
- Determine when and how ethanol increases PM
- Propose revised PMI to account for ethanol blending

Approach:

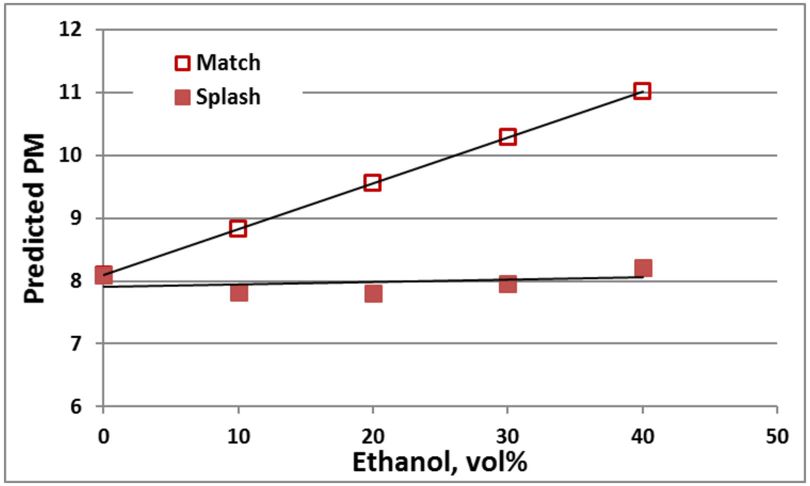
- Quantify PM emissions from a full-factorial fuel matrix
  - GM LNF engine modified to single cylinder
  - AVL Micro-soot sensor and dilution system

Experiment results and linear regression model highlight key factors controlling PM with increasing EtOH content in blends



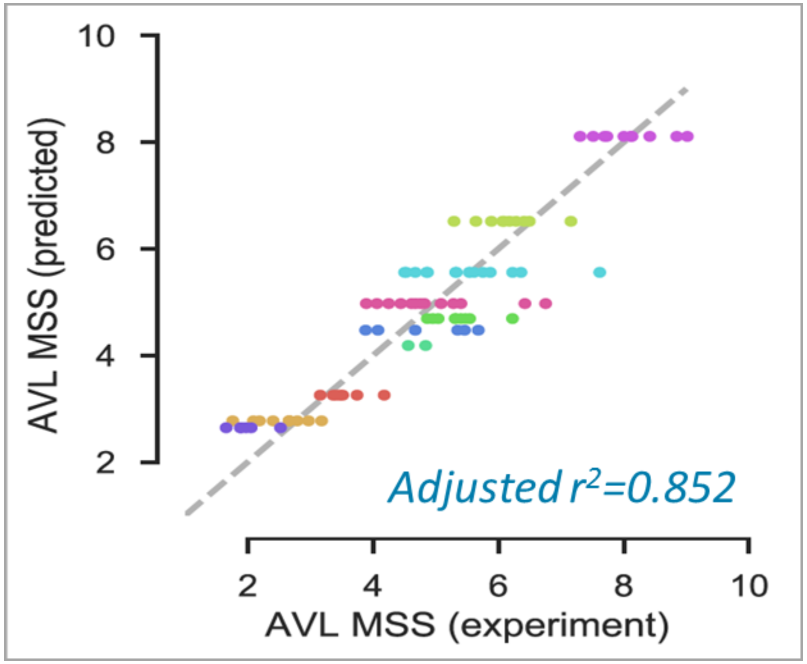


X1 + **0.044**{EtOH%} + **0.34**{Aro%} - **0.031**{AroP$_{vap}$}



- Significant PM variability with engine operating conditions
- Linear regression model shows:
  - – all 3 parameters statistically signif.
  - – aromatic content has largest effect
  - – splash blending dilutes aromatics, eliminating PM increase with EtOH

Regularized regression generates an improved model that accounts for parameter interactions



- Regularized regression approach reveals improved model based on variable combinations:

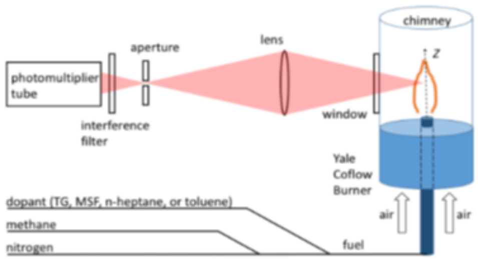
$$x1 + x2 * \left\{\frac{EtOH\% * Aro\%}{AroP_{vap}}\right\} + x3 * \left\{\frac{AroYSI * Aro\%}{AroMW}\right\}$$

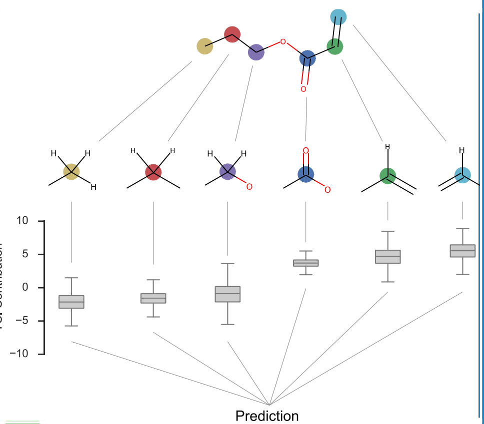
vapor pressure **sooting tendency**

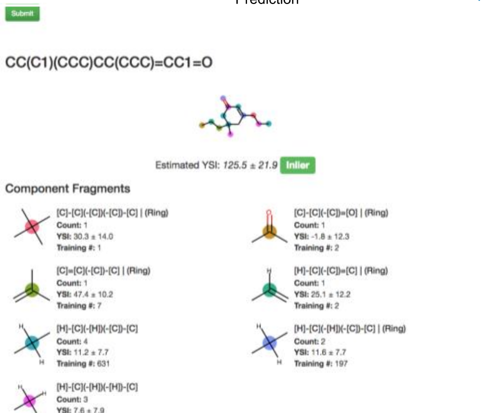
Conclusions:

- Ethanol can cause PM to increase with:
  - low P_{vap} aromatics
  - match blending
  - high engine loads & speeds
- Dilution of aromatics by ethanol splash blending eliminates PM increase
- Regularized regression used to generate a model that accounts for interactions between terms
- Revised model points toward strategy for modified PMI term

F.1.4.2 Predicting Sooting and Developing Quantum Skeletal Mechanisms for Soot and Autoignition (BETO funded)







Seonah Kim, Peter St. John (NREL); Charles McEnally, Lisa Pfefferle (Yale), Yuan Xuan (Penn State)

Relevance:

- Changes in fuel chemistry could have a significant impact on PM formation and emissions compliance
- Effective co-optimization requires fuel properties that correlate with soot formation tendency
- Yield Sooting Index (YSI) requires experimental measurements for every fuel

Objectives:

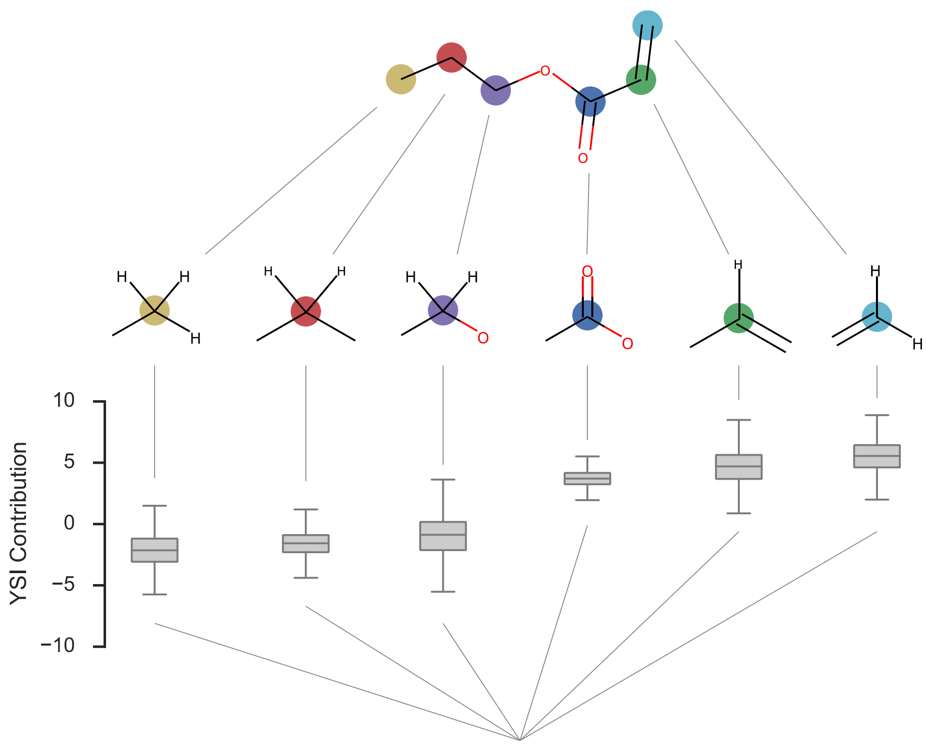
- Develop a fast fuel property screening tool that can predict YSI from molecular structures

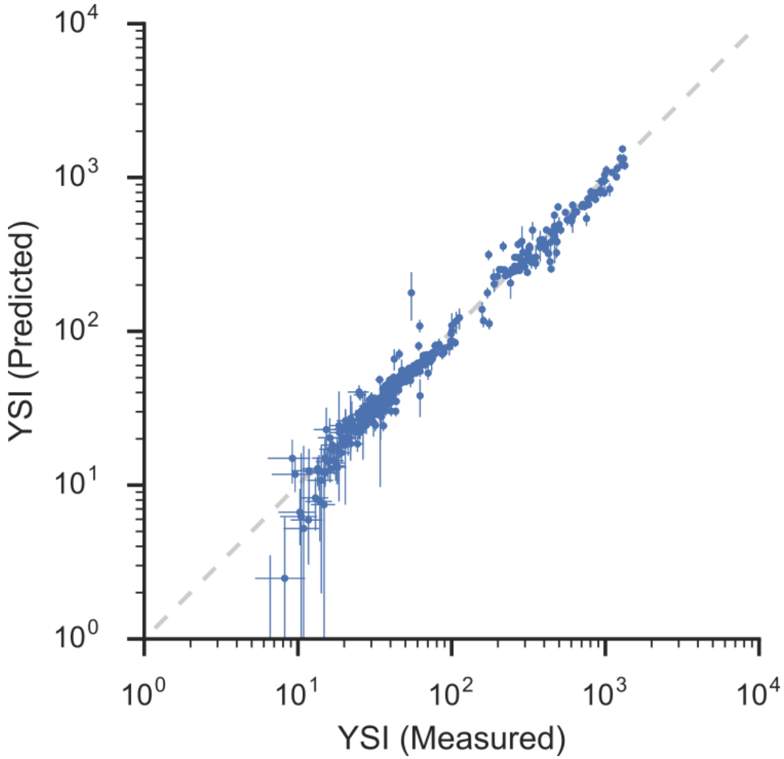
Approach:

- Apply machine learning techniques to develop Quantitative Structure-Property Relationship (QSPR) Models for YSI Prediction from measured YSI values and molecular structures for ~500 species

Quantitative structure-property relationship (QSPR) models for YSI prediction from machine learning

1. Input molecules are decomposed into individual carbon-type fragments
2. Bayesian linear regression is used to find the YSI contributions from each atom type
3. The final YSI prediction is a sum of each carbon in the molecule

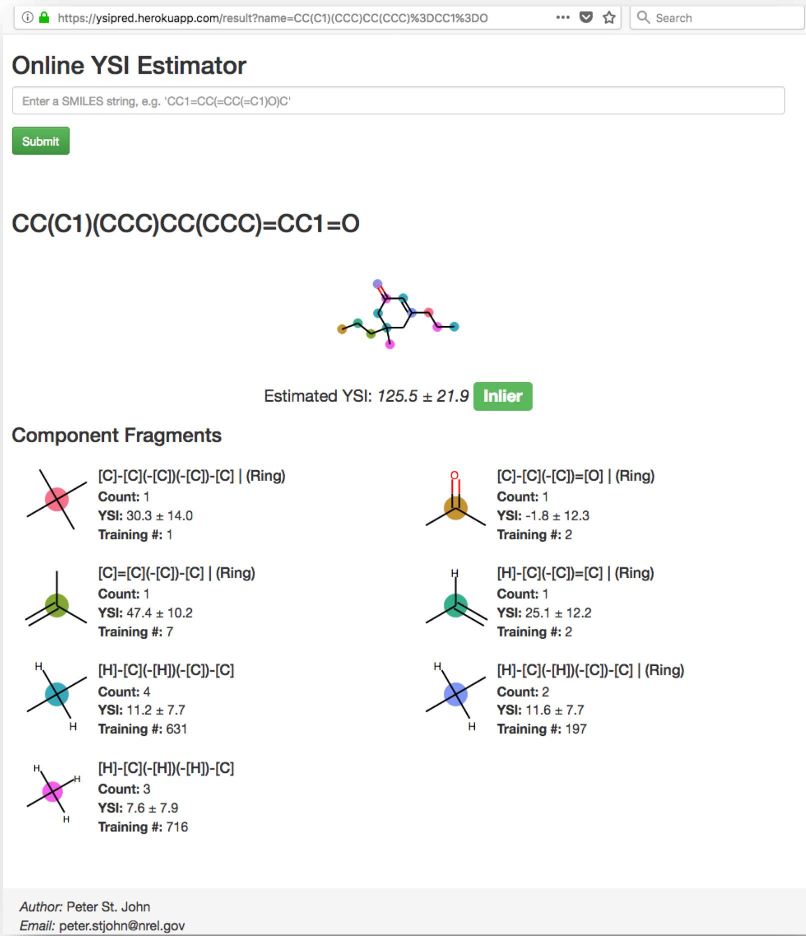




Regressed model is accurate across two orders of magnitude

Das and St. John *et al. Comb. Flame* (2018)

YSI screening tool now available through web app

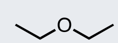
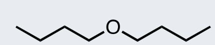
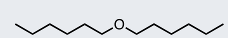
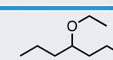
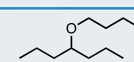


https://ysipred.herokuapp.com

Results:

- Developed YSI fuel property prediction tool
- Created Web app
- Generating insights into connection between structure, sooting tendency
- Working with other Co-Optima researchers to screen potential blendstocks based on YSI

FUEL PROPERTY SCREENING MD/HD

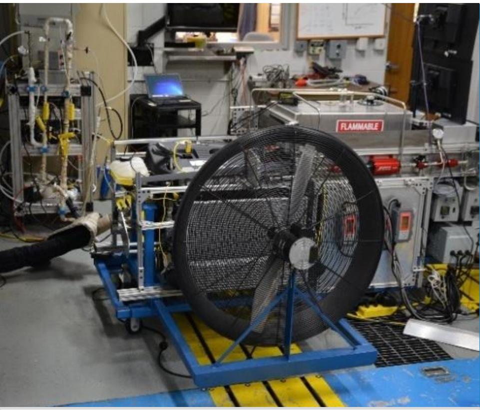
Ether Compound	Structure	CN	YSI	Melting Boiling (°C)	Flash Point (°C)	Lower HV (MJ/kg)	Water Solubility (g/L)
Diethyl ether		160	17 4.5	-116 41	-45	28.4	60.5
Dibutyl ether		115	39 5.2	-71 132	25	38.3	0.6
Dihexyl ether		118	65* 5.4	-26 224	77	Pending	<0.1
4-ethoxy heptane		64*	51* 5.7	-75 155	31*	Pending	Pending
4-butoxy heptane		76*	63* 5.7	-53 200	59*	Pending	Pending

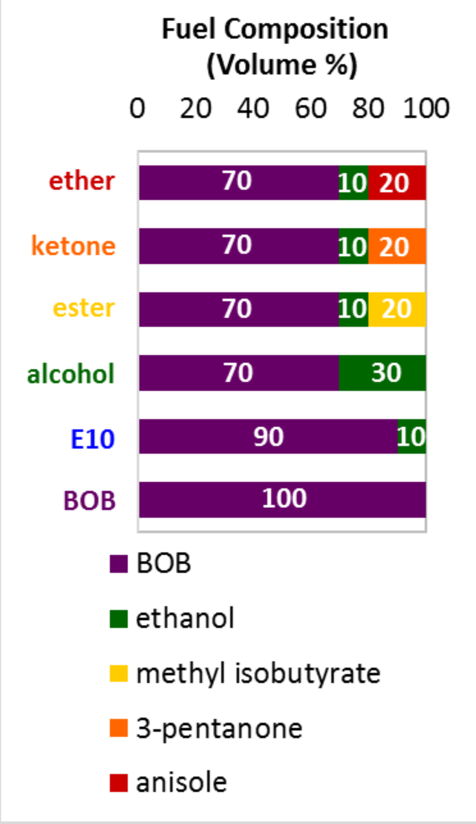
Collaboration with Derek Vardon (HPF)

Remaining challenges and future work for F.1.6.1 and F.1.4.2

Remaining Challenges	**Future Work** *(subject to change with funding levels)*
• PMI does not account for increase in PM for high ethanol concentrations with high P_{vap} aromatics	• Use results of regression analyses to modify PMI
• YSI is not directly linked to PM production from engines	• Develop correlative models for engine-level (Diesel and mixed-mode) sooting behavior prediction
• Lack of tools for predicting fuel properties based on molecular structure	• Expand YSI prediction tool-kit to other fuel properties (e.g., HoV, flash point)

E.1.3.5: Study Fuel Impacts on ACI PM Formation & Complete Study of Impact on GDI PM





Melanie Moses-DeBusk, John Storey, Sam Lewis, Maggie Connatser, Shean Huff and Eric Nafziger (ORNL)

Relevance:

- Advanced engines & fuels must meet emissions standards
- Ethanol can improve combustion, reduce PM
  - Do other oxygenates have similar effects?
- Cold start is a major source of PM, HC emissions
  - How will Co-Optima blendstocks affect gaseous HC speciation and PM composition?

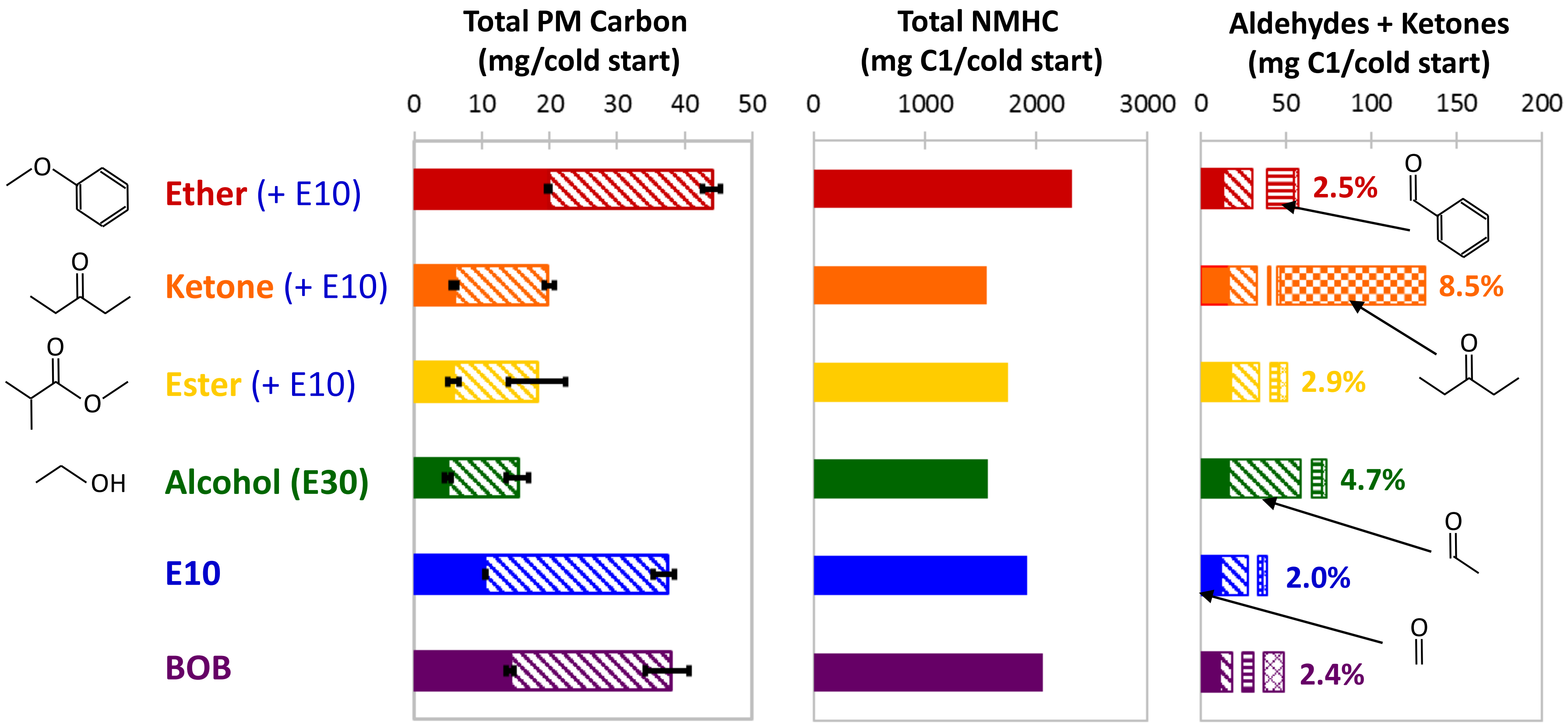
Objectives:

- Study impact of oxygenate chemistry on cold-start emissions

Approach:

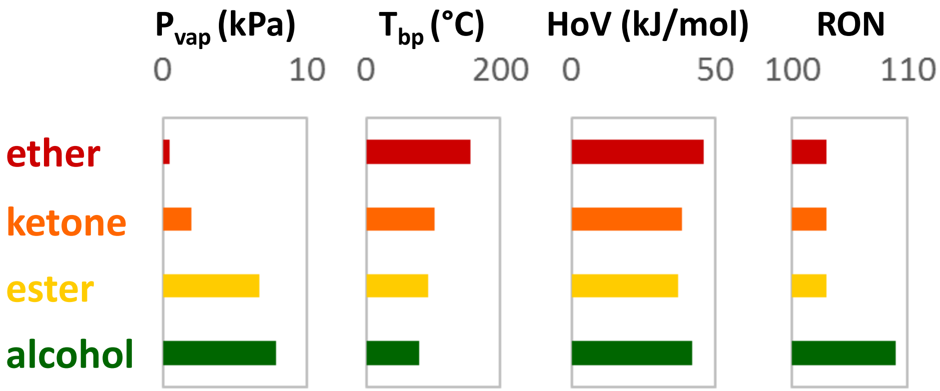
- Use force-cooled engine to allow multiple rapidly repeated cold start measurements in a single day
- Apply ORNL's extensive sampling and analysis capabilities to measure exhaust chemistry

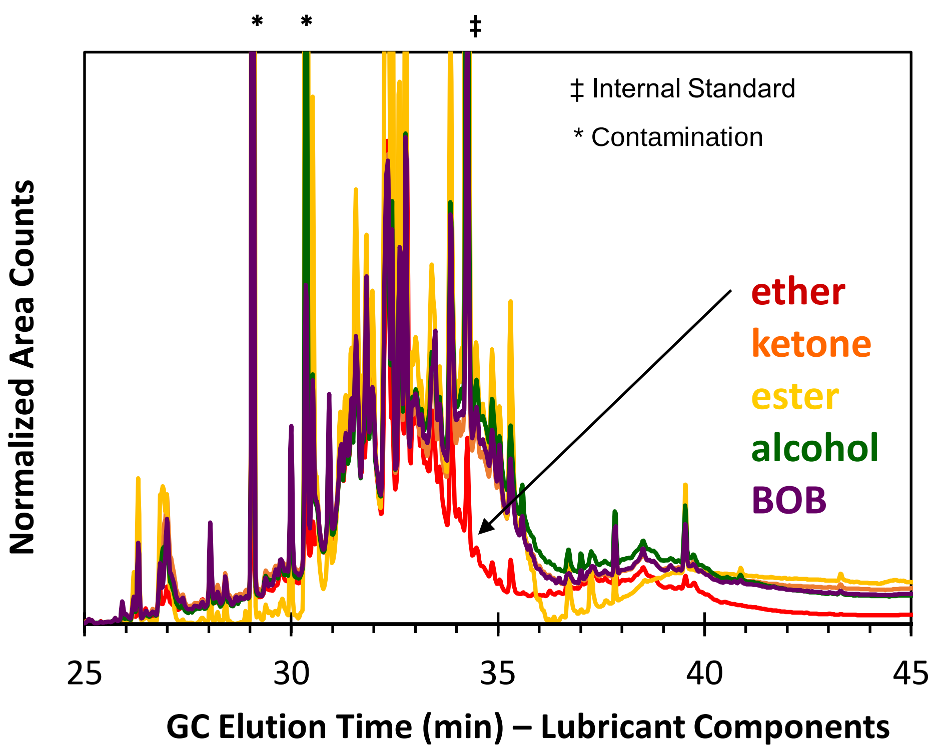
Chemistry of oxygenates in fuel blends impacts quantity and composition of PM and HC emissions from a boosted SI engine



- Oxygenate blends reduce total PM and NMHC emissions, but increase emissions of aldehydes and ketones (some of which are air toxics)
  - exception: anisole (aromatic ether) increases PM and NMHC
- Important to weigh trade-off of PM and THC reduction with HC specific impacts on emissions and aftertreatment systems

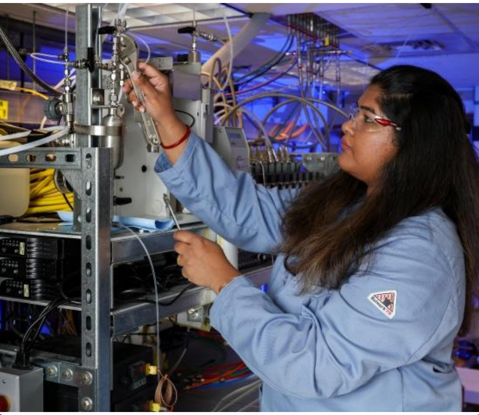
Thermal desorption of PM reveals interesting effects of oxygenates on PM composition and in-cylinder processes

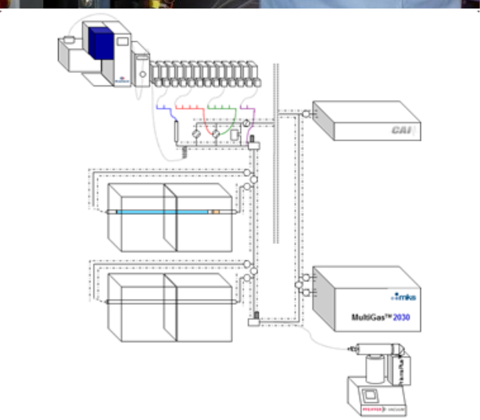




- Thermal desorption of HCs from GDI PM yields detailed OC composition information
- Majority of OC from lubricant components (elution time)
- Anisole results in different OC composition relative to all other fuels
  - change to in-cylinder processes
  - much lower P_{vap}, higher BP
- Similar detailed composition information could yield critical insights into fuel effects on ACI combustion strategies

E.1.3.1: Fuel Impacts on Emissions Control Performance & Durability





Josh Pihl, Sreshtha Sinha Majumdar, Todd Toops (ORNL)

Relevance:

- Co-Optimized engines + fuels still must meet emissions regulations
- Changes in fuel chemistry may affect catalyst performance, potentially impacting emissions control system compliance, fuel penalty, or cost

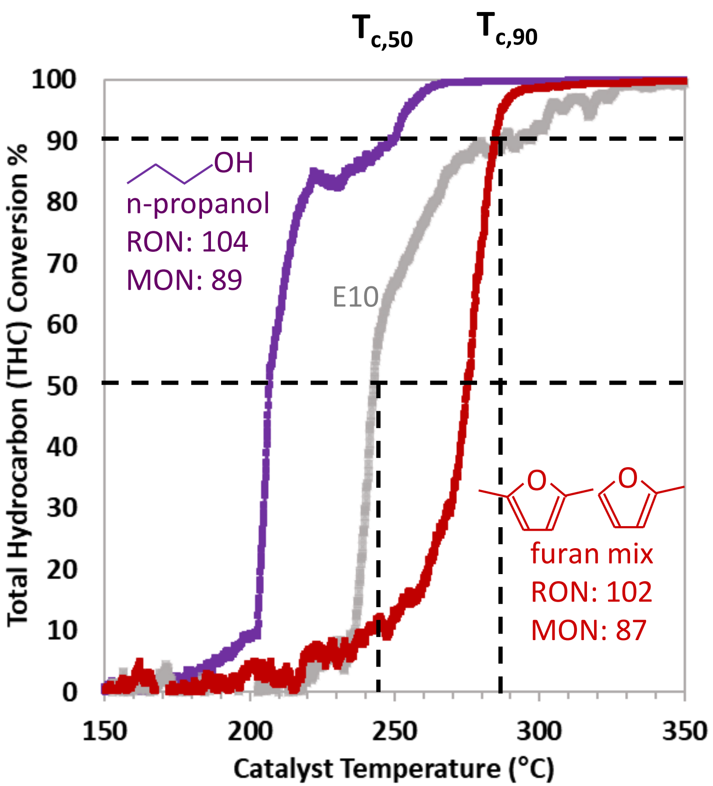
Objectives:

- Develop merit function terms that capture emissions control effects, measure associated fuel properties
- Identify challenges & opportunities from new fuels
  - catalyst light-off performance during cold start
  - catalyst poisoning by fuel impurities
  - NO SCR by oxygenates for lean NOx control

Approach:

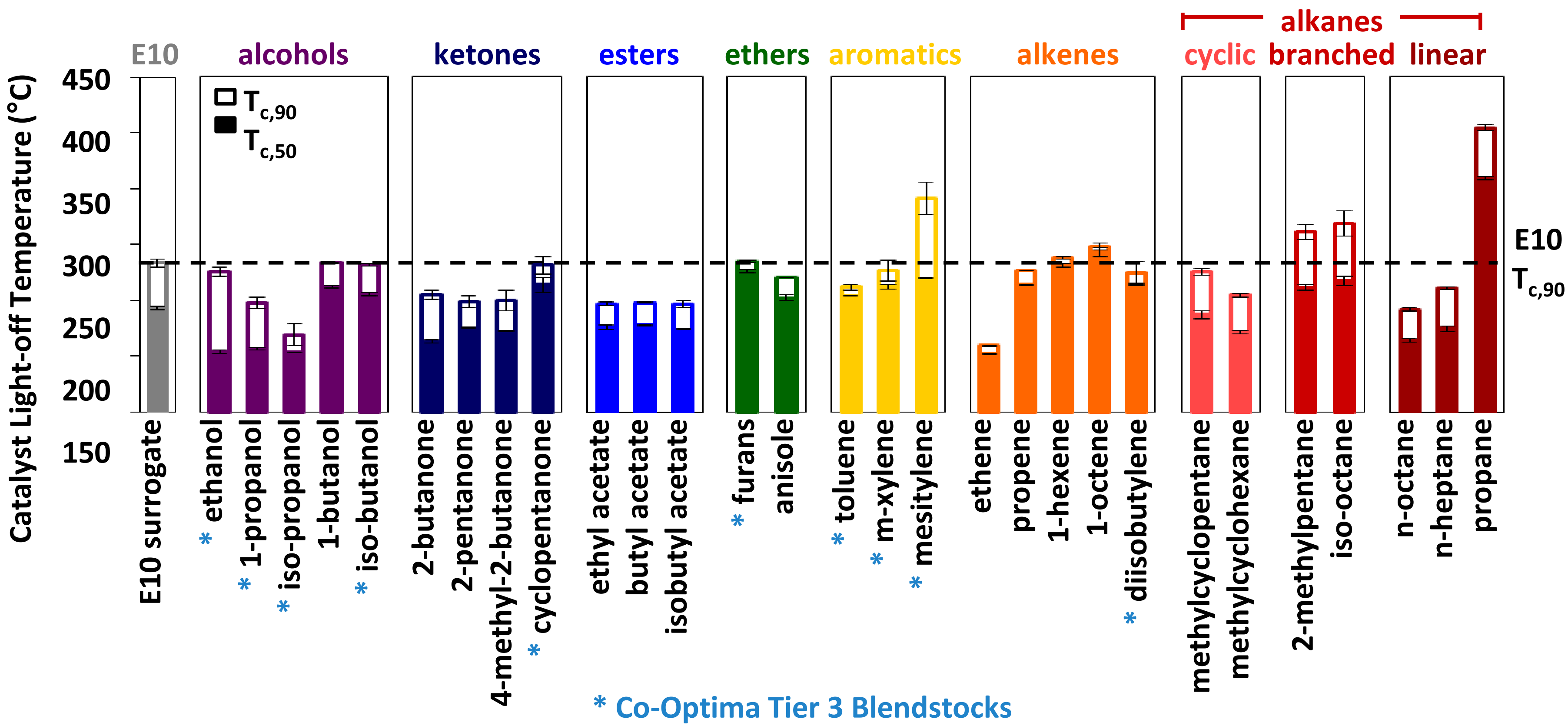
- Use synthetic exhaust flow reactors to measure the impacts of fuel chemistry changes on commercially relevant catalyst materials

Measured TWC light-off temperatures on a synthetic exhaust flow reactor to capture changes in cold start catalytic activity



- Boosted SI engines rely on TWCs to meet EPA emissions regulations
  - TWCs do not work when cold
  - nearly all emissions from SI engines occur during cold start
- Changes in fuel chemistry can change TWC light-off behavior
- Synthetic exhaust flow reactor experiments provide a means to measure light-off for a wide range of fuels
  - aged commercial TWC core sample
  - protocols developed by industry
- TWC light-off does not correlate with gaseous fuel reactivity (RON, MON)

Measured TWC light-off temperatures for 18 Co-Optima blendstocks and 12 conventional HC fuel components



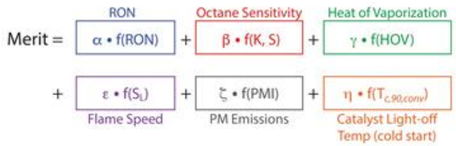
- Evaluated Co-Optima blendstocks, gasoline components, exhaust constituents, E10 surr.
  – most oxygenates light-off at lower Ts than E10
  – aromatics, alkenes tend to light-off at higher Ts than E10
- Observed interesting dependencies on chemical structure

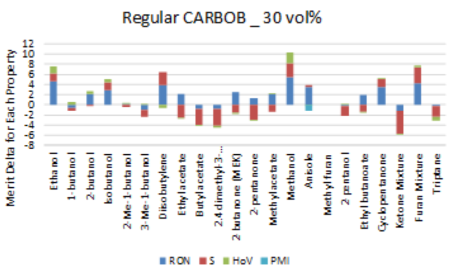
Ongoing work is focused on understanding fuel blends for boosted SI, but future efforts will shift to SI/ACI multimode operation

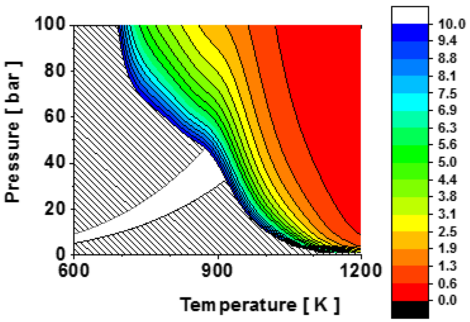
Remaining Challenges	**Future Work** *(subject to change with funding levels)*
• Link between individual blendstock catalytic light-off temperature and fuel blend reactivity has not been established	• Measure light-off temperatures for fuel mixtures containing Co-Optima blendstocks • Develop strategies for predicting blend light-off from individual components

• ACI creates emissions challenges:
    • high HC emissions
    • low exhaust Ts,
    • possible need for lean NOx control
• Potential mitigating or exacerbating effects of fuel chemistry on those challenges is not well understood
	• Investigate influence of fuel chemistry and engine operating parameters on soot formation pathways for ACI combustion
	• Measure detailed exhaust composition on SI/ACI and full-time ACI engine platforms running with relevant fuels
	• Identify potential emissions control architectures for SI/ACI and full-time ACI
	• Evaluate impact of Co-Optima blendstocks on performance of low T catalyst materials
	• Develop merit function terms that capture fuel effects on emissions control

E.2.3.1: Merit Function Development & Technical Roll-up







Chris Kolodziej (ANL), Paul Miles (SNL), Bob McCormick (NREL), Jim Szybist (ORNL)

Relevance:

- Co-Optimization of fuels and engines requires a quantitative link between fuel properties and engine performance parameters

Objectives:

- Develop merit functions for each combustion strategy in the Co-Optima program

Approach:

- Coordinate team discussions, literature surveys, and data mining efforts to identify quantitative links between fuel properties and engine performance
- Work with Co-Optima researchers to develop, validate, and refine merit function coefficients

Co-Optima SI merit function has been refined and published

Efficiency $\boxed{merit =}$ $\boxed{+\frac{(RON_{mix} - 91)}{1.6} - K\frac{(S_{mix} - 8)}{1.6}}$ Octane Index

$$+\frac{0.085[ON/kJ/kg_{mix}]\left(\left(HoV_{fuel}/(AFR_{stoich}+1)\right) - \left(415\,[kJ/kg_{fuel}]/(14.3[-]+1)\right)\right)}{1.6}$$
$$+\frac{\left(\left(HoV_{fuel}/(AFR_{stoich}+1)\right) - \left(415\,[kJ/kg_{fuel}]/(14.3[-]+1)\right)\right)}{15.38}$$

Heat of Vaporization

$\boxed{+\frac{(S_{Lmix} - 46[cm/s])}{5.4}}$ Flame Speed

$\boxed{-H(PMI - 1.6)[0.7 + 0.5(PMI - 1.4)]}$ Particulate

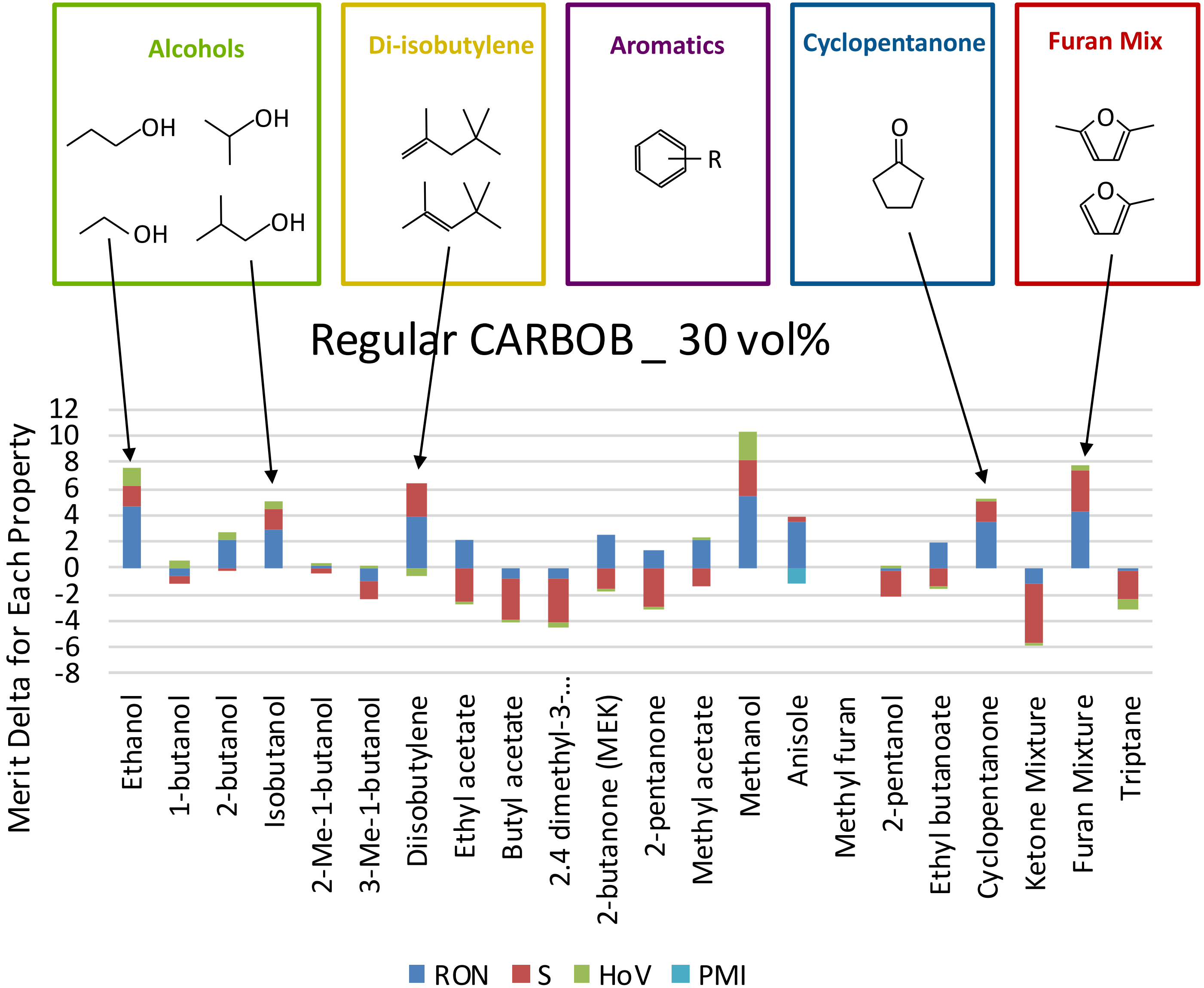
$\boxed{+0.008°C^{-1}(T_{c,90,conv} - T_{c,90,mix})}$ Catalyst Light-off

- Builds on a century of fuels research and decades of investigations into fuel effects on SI engine efficiency
- Provides quantitative link between fuel properties and engine efficiency for use in screening fuel candidates
- Merit function report[1] and fuel properties database[2] both available online

[1]**"Co-Optimization of Fuels & Engines Efficiency Merit Function for Spark-Ignition Engines" Report:**
https://www.energy.gov/sites/prod/files/2018/02/f48/Co-Optima%20Merit%20Function%20Report%2067584_2.pdf

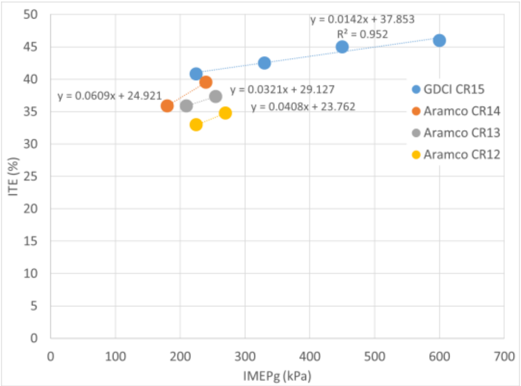
[2]**Co-Optima Fuel Property Database:**
https://fuelsdb.nrel.gov/fmi/webd/FuelEngineCoOptimization

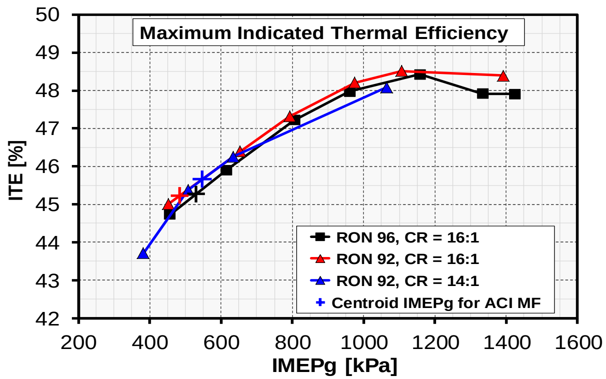
SI merit function was used to identify promising categories of blendstocks

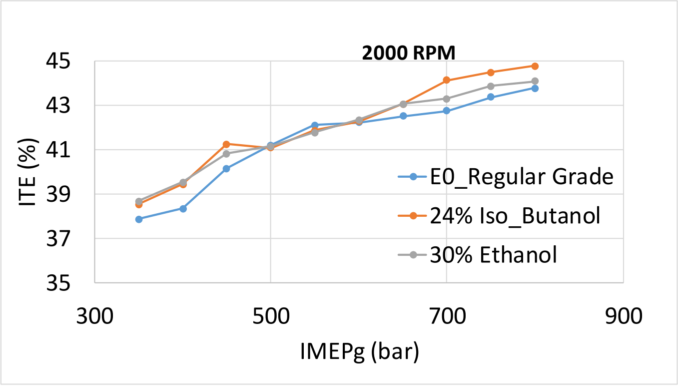


Preliminary efforts to develop ACI merit function revealed a need for further understanding of fuel effects on ACI

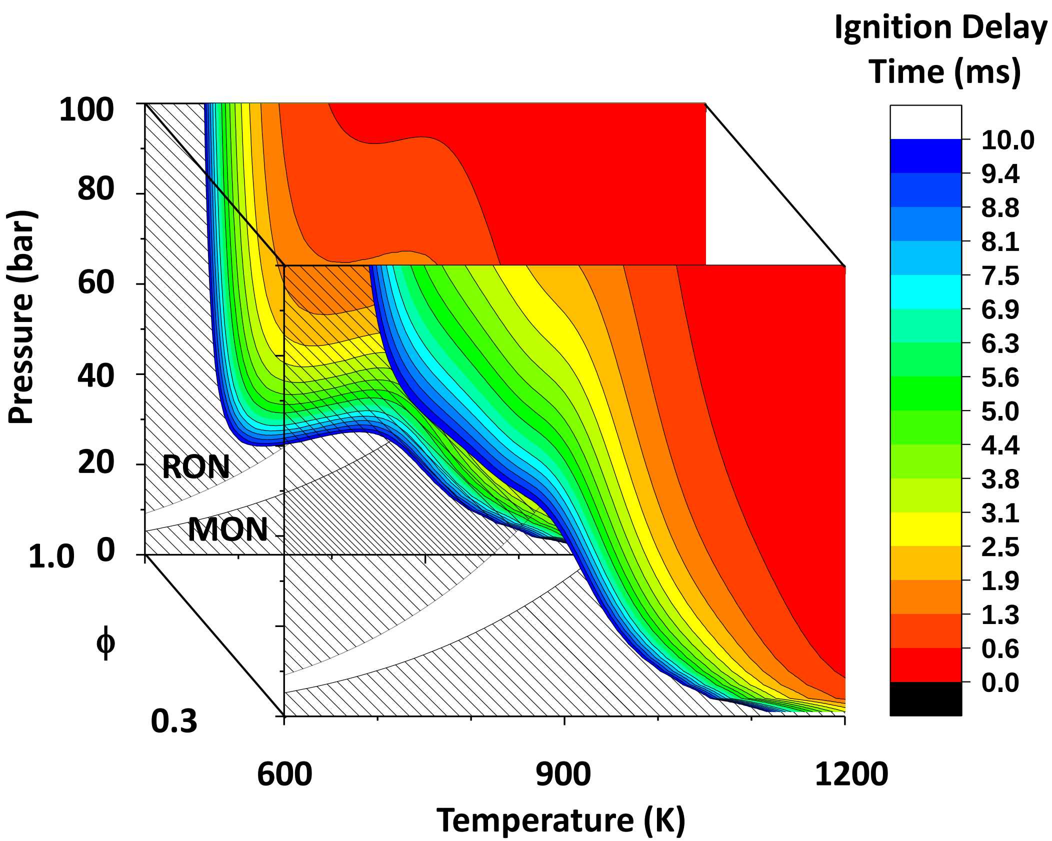
- Attempted to build a similar merit function for ACI combustion modes
- Preliminary analysis of literature and national lab data focused on effect of RON on ACI engine efficiency
  - RON had little to no effect on indicated thermal efficiency for ACI engines
- Going forward, focus will shift to fuel effects on combustion system operability (e.g., load range)
- Separate merit functions may be needed for different ACI modes
  - operate in different P/T/ϕ regimes
  - autoignition chemistry for a single fuel can vary significantly with P/T/ϕ







Current focus: understand autoignition chemistry over wider P/T/ϕ space for range of fuels and correlate with ACI engine performance



- Expand understanding of autoignition chemistry to lean equivalence ratios for a wide range of fuels
  - kinetic mechanisms
  - kinetics measurements
  - simulations
  - engine experiments
- Correlate engine performance with autoignition behavior
- Identify fuel properties that are predictive of autoignition behavior
- Develop ACI merit function(s)

Collaborations & partnerships

- Collaboration across:
  - 9 DOE national laboratories
  - 13 universities
  - 2 DOE offices
- Stakeholders (145 individuals from 86 organizations):
  - external advisory board (advising national labs, not DOE)
  - monthly telecons with technical and programmatic updates
  - one-on-one meetings and conference presentations
- Projects presented to the ACEC Tech Team and at the semi-annual AEC program review meetings

- NREL collaborates with Yale and Penn State on YSI
- ORNL uses protocols developed by the ACEC Tech Team Low Temperature Aftertreatment Working Group and shares results with the aftertreatment community though the CLEERS organization

Response to reviewer comments

Reviewer Comments	Response
• "one emissions aspect that appears to be missing is assessing the formation of toxics such as formaldehyde and acetaldehyde"	• Aldehydes are included in the standard exhaust speciation work at ORNL, and results were included in this presentation
• "catalytic light-off temperatures for pure components are interesting, but… need to see light-off behavior in blends"	• Blend light-off experiments are ongoing, but were not completed in time for inclusion in this talk
• "collaboration with industry appears to be very limited" • "project needs more involvement from aftertreatment suppliers"	• Projects have been presented at ACEC Tech Team meetings • Collaborations with aftertreatment suppliers will increase with change in focus to ACI and low T catalysts
• "additional work on low-temperature catalysts is critical for future low-temperature combustion engines and should be expanded."	• Catalyst development is the focus of other projects, but fuel effects on oxidation catalysts and low T traps will be investigated going forward

Summary

Relevance:

- We need to understand how fuel chemistry impacts exhaust composition and performance of emission control devices to predict the effects of Co-Optima blendstocks on emissions compliance

Approach:

- Utilize unique lab capabilities to develop a fundamental understanding of how changes in fuel chemistry impact emissions, emission control devices, and engine performance

Accomplishments:

- Developed a regression model for PM production from ethanol fuel blends containing low Pvap aromatics that points to a revised PMI calculation
- Developed a YSI fuel property prediction tool and created a web app
- Quantified effects of changing fuel chemistry on exhaust composition (PM, NMOG speciation) from a boosted SI engine during cold start
- Measured catalyst light-off temperatures for a wide range of fuel components to support evaluation of the emissions control term in the LD merit function

Collaborations:

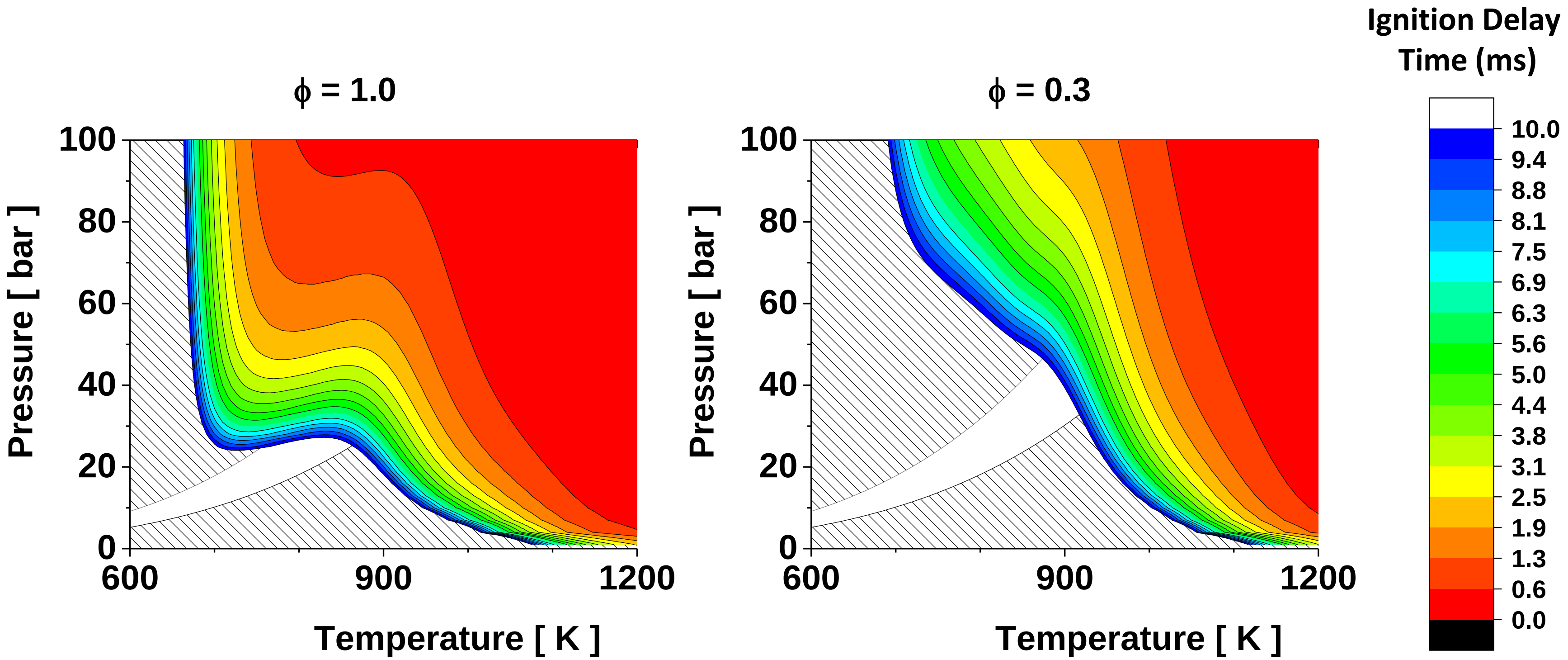
- 9 national labs, 13 universities, 145 stakeholders from 86 organizations, ACEC Tech Team, CLEERS

Future Work (subject to change based on funding levels):

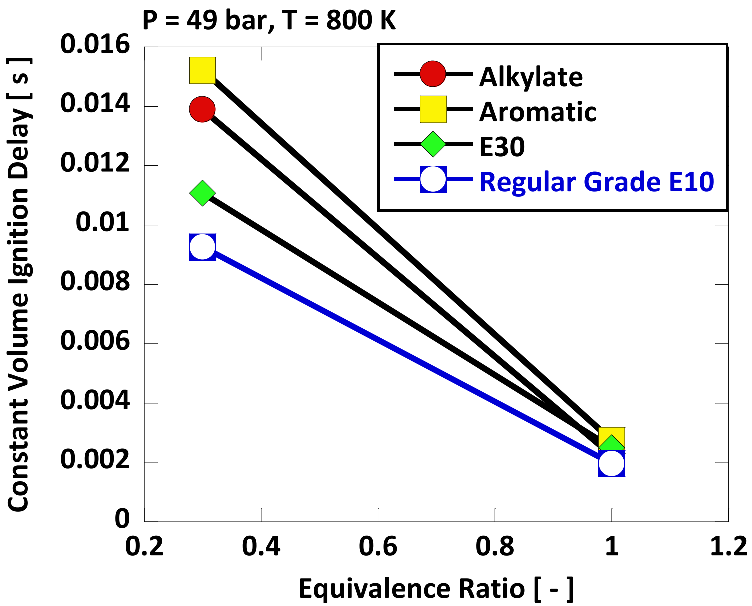
- Use results of regression analyses to modify PMI
- Develop correlative models for engine-level (Diesel and mixed-mode) sooting behavior prediction
- Measure detailed exhaust composition on SI/ACI and ACI engine platforms running with relevant fuels
- Evaluate impact of Co-Optima blendstocks on performance of low T catalyst materials
- Expand understanding of autoignition chemistry to lean equivalence ratios for a wide range of fuels

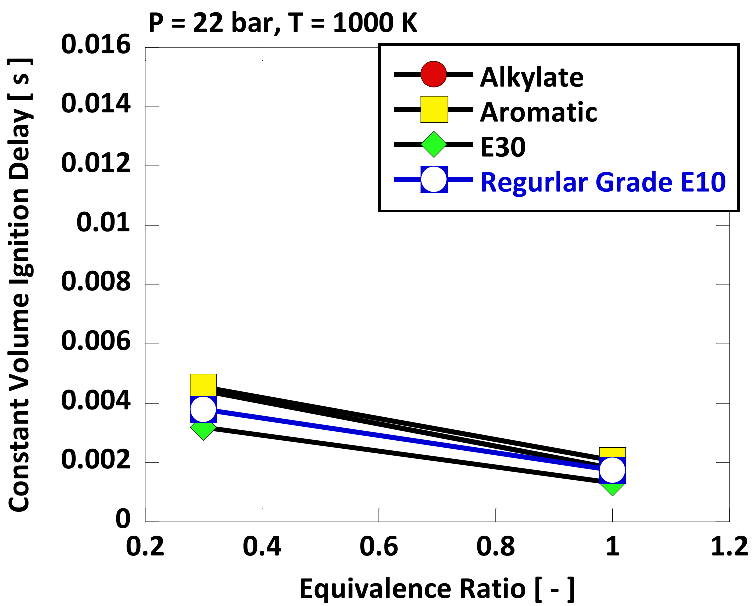
Technical Back-Up Slides

Autoignition behavior changes with equivalence ratio



Phi sensitivity is dependent on fuel as well as pressure temperature operating condition





- At a high P, low T condition, all fuels exhibit phi-sensitivity.
- Ethanol and regular grade gasoline exhibit less than aromatic and alkylate based on the kinetics.

- At a low P, high T condition, phi-sensitivity is significantly reduced for all fuels.